

FORM PTO-1590
(11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

CWR 2 0269

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/914517

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/US00/06724

15 MARCH 2000

15 MARCH 1999

TITLE OF INVENTION

METAL SPONGES FOR RAPID SURFACE CHEMICAL REACTIONS

APPLICANT(S) FOR DO/EO/US

WELSCH, Gerhard et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☒ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☐ Other items or information:

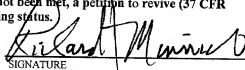
U.S. APPLICATION NO. (If known) 09/014517	INTERNATIONAL APPLICATION NO. PCT/US00/06724	ATTORNEY'S DOCKET NUMBER CWR 2 0269
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21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY																							
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$ 690.00																							
<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <th style="width:20%;">CLAIMS</th> <th style="width:20%;">NUMBER FILED</th> <th style="width:20%;">NUMBER EXTRA</th> <th style="width:20%;">RATE</th> <th style="width:20%;">\$</th> </tr> <tr> <td>Total claims</td> <td>27 - 20 =</td> <td>7</td> <td>x \$18.00</td> <td>\$ 126.00</td> </tr> <tr> <td>Independent claims</td> <td>4 - 3 =</td> <td>1</td> <td>x \$80.00</td> <td>\$ 80.00</td> </tr> <tr> <td colspan="4">MULTIPLE DEPENDENT CLAIM(S) (if applicable)</td> <td>+ \$270.00</td> </tr> <tr> <td colspan="4">TOTAL OF ABOVE CALCULATIONS =</td> <td>\$ 206.00</td> </tr> </table>	CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	Total claims	27 - 20 =	7	x \$18.00	\$ 126.00	Independent claims	4 - 3 =	1	x \$80.00	\$ 80.00	MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$270.00	TOTAL OF ABOVE CALCULATIONS =				\$ 206.00	\$	
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<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				+ \$ (448.00)																							
SUBTOTAL =				\$ 448.00																							
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$																							
TOTAL NATIONAL FEE =				\$																							
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$																							
TOTAL FEES ENCLOSED =				\$ 448.00																							
				Amount to be refunded: \$																							
				charged: \$																							

- a. ☒ A check in the amount of \$ 448.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
 A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment to Deposit Account No. 060309. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card
 information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:
Richard J. Minnich, Esq.
Pay, Sharpe, Fagan, Minnich & McKee, LLP
1100 Superior Avenue, 7th Floor
Cleveland, OH 44114-2581


 SIGNATURE
Richard J. Minnich
 NAME
24,175
 REGISTRATION NUMBER

09/014517 042802 206240 154166

U.S. PATENT AND TRADEMARK OFFICE

INTERNATIONAL APPLICATION NO.
PCT/US00/06724ATTORNEY'S DOCKET NUMBER
CWR 2 026921. ☐ The following fees are submitted:

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but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

\$ 690.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS NUMBER FILED NUMBER EXTRA RATE \$

Total claims 27 -20 = 7 x \$18.00 \$ 126.00

Independent claims 4 -3 = 1 x \$80.00 \$ 80.00

MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$270.00 \$

TOTAL OF ABOVE CALCULATIONS = \$ 206.00

☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2. \$ (448.00)

SUBTOTAL = \$ 448.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
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Amount to be
refunded: \$

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A duplicate copy of this sheet is enclosed.
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overpayment to Deposit Account No. 060308. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card
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SIGNATURE

Richard J. Minnich

NAME

24,175

REGISTRATION NUMBER

09/914517

JC03 Rec'd PCT/STO 14 SEP 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Gerhard Welsch et al.
 Serial No. : Unknown
 Filed : Herewith
 Title : METAL SPONGES FOR RAPID SURFACE
 CHEMICAL REACTIONS
 Attorney Docket : CWR 2 0269

Assistant Commissioner For Patents
 Washington, D.C. 20231

PRELIMINARY AMENDMENT

Dear Sir:

Prior to substantive examination of the above-identified patent application, please amend the application as follows:

IN THE CLAIMS:

Please amend claims 4, 5, 6, 7, 8, 9, 10, 12, 14, 17 as follows:

4. The battery of claim 2, further characterized by the substrate and the electrically conductive sponge being formed from the same material.

5. The battery of claim 2, further characterized by the substrate including a metal selected from the group consisting of silver, copper, and aluminum.

6. The battery of claim 2, further characterized by the sponge metal being in the form of particles attached to the substrate.

CERTIFICATE OF MAILING

I hereby certify that this Preliminary Amendment is being deposited with the United States Postal Service as Express Mail No. EL95214391DVS, addressed to: Assistant Commissioner For Patents, Washington, D.C. 20231, on September 14, 2001.

P. Stepka
 Pamela S. Stepka

09/914517 "PCT/STO" 14 SEP 2001

7. The battery of claim 2, further characterized by the sponge material being in the form of a layer of sponge grown on the substrate.

8. The battery of claim 1, further characterized by the at least one of the anode and cathode comprising a plurality of thin layers of the electrically conductive sponge material.

9. The battery of claim 1, further characterized by the electrically conductive sponge material including an element selected from the group consisting of copper, silver, gold, aluminum, and combinations thereof.

10. The battery of claim 1, further characterized by the electrically conductive sponge material defining dendrites.

12. The battery of claim 10, further characterized by the at least one of the anode and cathode including at least one substrate layer and wherein the dendrites extend from the substrate.

14. The battery of claim 1, further characterized by the sponge materials being coated with an electrically conductive material.

17. The method of claim 15, further characterized by the step of growing the sponge including:

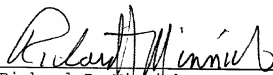
reducing a compound to its elemental form, the elemental form occupying a smaller volume than the compound such that an open porous structure is formed.

22. The method of claim 20, further characterized by the sponge material comprising an element selected from the group consisting of Mg, Al, Si, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Cv, Ag, Ti, Te, Tl, Pb, Bi, and alloys thereof.

REMARKS

It is respectfully submitted that the subject application is now in better condition for examination.

Respectfully submitted,



Richard J. Minnich
Reg. No. 24,175

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2025-04-27 14:51:00

VERSION WITH MARKINGS SHOWING CHANGES MADE

4. The battery of [either one of preceding claims 2 or 3] claim 2, further characterized by the substrate and the electrically conductive sponge being formed from the same material.

5. The battery of [either any one of preceding claims 2-4] claim 2, further characterized by the substrate including a metal selected from the group consisting of silver, copper, and aluminum.

6. The battery of [any one of preceding claims 2-5] claim 2, further characterized by the sponge metal being in the form of particles [(114, 164, 190, 192)] attached to the substrate.

7. The battery of [any one of preceding claims 2-5] claim 2, further characterized by the sponge material [(16,86,98,114,120)] being in the form of a layer [(122,204)] of sponge grown on the substrate.

8. The battery of [either any one of preceding claims 1-7] claim 1, further characterized by[:]
the at least one of the anode [(10,160,182,202)] and cathode [(12,168,184,208)] comprising a plurality of thin layers [(166)] of the electrically conductive sponge material.

9. The battery of [any one of preceding claims 1-8] claim 1, further characterized by[:]
the electrically conductive sponge material including an element selected from the group consisting of copper, silver, gold, aluminum, and combinations thereof.

10. The battery of [any one of preceding claims 1-9] claim 1, further characterized by the electrically conductive sponge material defining dendrites [(18,100)].

12. The battery of [either one of claims 10 and 11] claim 10, further characterized by the at least one of the anode and cathode including at least one substrate layer [(14,82,206)] and wherein the dendrites [(18,100)] extend from the substrate.

14. The battery of [any one of claims 1-13] claim 1, further characterized by the sponge materials being coated with an electrically conductive material [(39)].

17. The method of [either one of claims 15 and 16] claim 15, further characterized by[:]
the step of growing the sponge including:
reducing a compound [(122)] to its elemental form [(126)],
the elemental form occupying a smaller volume than the compound
such that an open porous structure is formed.

22. The method of [either one of claims 20 and 21] claim 20, further characterized by the sponge material comprising an element selected from the group consisting of Mg, Al, Si, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Cv, Ag, Ti, Te, Tl, Pb, Bi, and alloys thereof.

METAL SPONGES FOR RAPID SURFACE-CHEMICAL REACTIONS

Background of the Invention

The present invention relates to the surface chemistry arts. It finds particular application in conjunction with reaction surfaces formed from metal sponges having a high, readily accessible surface area for conducting chemical reactions thereon, and will be described with particular reference thereto. It should be appreciated, however, that the invention is also applicable to a variety of applications in which a high accessible surface area to volume ratio is beneficial.

Many chemical reactions involve surface reactions which take place on the surface of one or more of the reactants. Devices such as batteries, catalysts, gas sensors, fuel cells, and heat exchangers, for example all depend on chemical reactions taking place at a surface. For such reactions, the reaction rate is heavily dependent on the available surface at which the reactants can interact.

For optimum efficiency of such devices, it is desirable for the reactants to be supplied to the surface, and the reaction products drawn from the surface with little resistance. For example, a battery containing an anode, an electrolyte, and a cathode will benefit from an anode having a high, accessible surface area for an oxidation reaction to take place at a high rate. Similarly, the battery will benefit from a cathode of high accessible surface area for a rapid reduction reaction. This results in a high power output for the battery.

Conventionally, batteries are made from a number of interleaved plates which provide the anode and cathode. The thickness of the plates is limited because, below a certain thickness, the plates cease to be rigid enough to maintain a desired spacing.

Metallic sponges provide an opportunity for increasing the surface area over conventional electrode materials. Sponges of titanium, such as those produced by the Hunter and Kroll processes, have relatively large surface areas. However, surface areas may

not be maximized since a considerable portion of the surface is inaccessible, being fully enclosed by the sponge.

The present invention provides for a new and improved reaction surface formed from a sponge which overcomes the above-referenced problems and others.

5

Summary of the Invention

In accordance with one aspect of the present invention a battery comprising an anode, a cathode, and an electrolyte therebetween is provided. The battery is characterized by at least one of the anode and cathode comprising an electrically conductive
10 sponge material.

In accordance with another aspect of the present invention, a method of conducting a reaction on a surface is provided. The method includes forming the surface, contacting the surface with a reactant, and allowing the reaction to take place. The method is characterized by the step of forming the surface including growing a sponge material
15 having a plurality of open pores which are accessible to the reactant.

One advantage of the present invention is that reaction surfaces with large surface areas per unit mass are formed, thereby enabling the size of a device to be reduced.

Another advantage of the present invention is that it provides numerous, short flow paths for efficient transport of reactants and reaction products.

20 Still further advantages of the present invention will become apparent to those of ordinary skill in the art upon reading and understanding the following detailed description of the preferred embodiments.

Brief Description of the Drawings

25 The invention may take form in various components and arrangements of components and in various steps and arrangements of steps. The drawings are only for purposes of illustrating a preferred embodiment, and are not to be construed as limiting the invention.

FIGURE 1 is a side sectional view of a battery incorporating a directionally-
30 grown sponge material according to a first embodiment of the present invention;

FIGURE 2 is a schematic view of the substrate and dendrites of FIGURE 1;

FIGURE 3 is a schematic view of an alternative embodiment of the substrate

and dendrites of FIGURE 1;

FIGURE 4 is a perspective view of the substrate and dendrites of FIGURE 1;

FIGURE 5 is a schematic view of a system for chemically forming directionally grown sponges according to the present invention;

FIGURE 6 is a schematic view of the system of Figure 5 during the distillation phase;

FIGURES 7A, 7B, and 7C are side schematic views to show the progressive growth of a directional sponge by a solidification method;

FIGURES 8 and 9 are schematic views of a ribbon extrusion system to show the growth of a dendritic sponge by the solidification process and the extrusion of a ribbon;

FIGURE 10 is a side schematic view to show an alternative embodiment of a ribbon extrusion system;

FIGURES 11A, 11B, 11C, and 11D are schematic views of a metal substrate A) prior to oxidation, B) after oxidation, C) after partial reduction, and D) after complete reduction of the oxide film;

FIGURE 12 is a side sectional view of a battery incorporating a non-directional sponge material according to a second embodiment of the present invention;

FIGURE 12 is a side sectional view of a battery incorporating a non-directional sponge material according to a second embodiment of the present invention;

FIGURE 13 is a side sectional view of a battery incorporating a non-directional sponge material according to a third embodiment of the present invention;

FIGURE 14 is a side sectional view of a battery incorporating a non-directional sponge material according to a fourth embodiment of the present invention; and

FIGURE 15 is a side sectional view of a battery incorporating a non-directional sponge material according to a fifth embodiment of the present invention.

Detailed Description of the Preferred Embodiments

Reaction surfaces with a large internal surface area are produced from metallic sponge. The sponges are formed by directional growth of a dendritic sponge on a suitable substrate or non-directional growth of a sponge. The sponges of the present invention have a large specific surface area (surface area per unit volume). For dendritic

sponges, that is sponges in which separate dendrites are attached to a common substrate or backbone, the specific surface area can be calculated approximately, according to the general formula:

$$\text{Specific surface area} = \frac{\text{Dendrite circumference} \times \text{Volume of Sponge Material}}{\text{Dendrite cross sectional area}}$$

- For example, a sponge with cylindrical dendrites of 100 nm in diameter has
 10 a specific surface area of $40 \text{ m}^2/\text{cm}^3$. By way of comparison, a solid of 1 cm^3 has a specific surface area of about $0.0006 \text{ m}^2/\text{cm}^3$.

The rate of a chemical reaction which takes place on a surface follows the formula:

$$\text{Rate of reaction} = \frac{\text{Reacted substance}}{\text{Volume} \times \text{Time}}$$

- The finer the dendrites, the larger will be the surface area, and the faster the
 20 rate of reaction on the surface.

It is important, however, for the surface area to be easily accessible to the mobile reactants, such as an electrolyte or a reacting gas, and provide a route for transport of reaction products away from the surface. Accordingly, both the flow paths provided by inter-dendritic pores and the conduction paths through the dendrites themselves are
 25 preferably short in order to provide low resistance to such movement. The short flow paths are provided by:

- a) providing a sponge with a directional structure. The inter-dendritic pores are aligned for short flow paths, and the dendrites are also aligned for short conduction paths; or,
- 30 b) providing a geometrical arrangement of a non-directional sponge in the form of thin layers which have numerous, short flow paths for access of electrolytes and/or reactants. For electrical applications, such as in batteries, the layers are preferably backed by a material with a high electrical conductivity.

Directional sponges and geometrical arrangements of thin layers of non-

directional sponges are particularly suited to providing a highly accessible surface for rapid transport of mobile reactants and products, ions in an electrolyte, or conduction of electrons.

Suitable materials for the sponge include aluminum, beryllium, carbon (graphite and other forms), cadmium, calcium, cesium, chromium, copper, germanium, gold, iron, lead, lithium, magnesium, manganese, nickel, niobium, platinum, potassium, sodium, silicon, silver, tantalum, titanium, vanadium, zinc, zirconium, or alloys of these metals. The choice of material will depend on the type of reaction for which the reaction substrate is to be used. For electrical applications, such as batteries, the sponge material is electrically conductive. For catalysts, the sponge material is preferably one which is capable of catalyzing the reaction.

The reaction surface can be formed in a number of ways, as will be discussed in detail below. It may be formed entirely from the sponge material, as in the case of an extruded dendritic sponge formed by a solidification method. Or the reaction surface may comprise a substrate material on which the sponge is either grown or attached by sintering, or other suitable method. The sintering method is particularly suited to forming reaction surfaces from particles of non-directional sponge, although it can also be used with directional sponges.

For some applications, the sponge may have its surface coated with a layer of a different material. For example, for catalytic uses, the sponge may be formed from an economical base material and coated with a thin layer of a catalyst material to provide a large surface area of the catalyst.

The reaction surfaces find application in a wide variety of devices, including catalysts, fuel cells, gas sensors, heat exchangers, and electrode materials for batteries. All of these applications benefit from having a large surface area and ease of access to and from the surface, derived from relatively short pathways or pores.

Reaction surfaces employing the two types of sponges, directional and non-directional, will now be described in greater detail. By way of example, the use of the reaction surface as an electrode in a battery will be shown, although it should be appreciated that both sponge types are suited to other applications, such as catalysts, fuel cells, and the like.

Reaction Surfaces Employing Directionally-Grown Sponges

Reaction surfaces employing directionally-grown, dendritic sponges have large accessible surface areas and short flow paths. The dendrites are preferably very fine, preferably having a width of about 30 micrometers or less, and more preferably of 1 micrometer or less, down to a few nanometers. The extreme fineness of the dendritic structure provides a high surface area (up to several hundred m^2/cm^3) on which the chemical reaction takes place. The inter-dendritic spaces or pores preferably have a pore size of 30 micrometers or less, more preferably of 300 nm or less.

The dendrites are directionally grown on a substrate. The substrate may be in the form of a ribbon, wire, cast structure or sheet. Alternatively, the substrate may be extruded along with the dendrites. The substrate provides the sponge with structural stability and, where desired, electrical conduction. The substrate may be formed from the same material as the sponge, or a different material. Substrates of silver, copper or aluminum are preferred for applications requiring electrical conduction.

One preferred embodiment of the reaction surface comprising dendritic sponge is an anode or cathode material in a battery. With reference to FIGURE 1, a battery 1 includes an anode 10 and a cathode 12, which both utilize the reaction surface. Specifically, the anode and the cathode are formed from inter-digitated sheets of foil 14 having a thickness of about 10 μm , or greater. The foil acts as a skeleton or substrate for a dendritic sponge material 16. The sponge material includes numerous dendrites 18 which extend from the substrate surface.

An electrolyte 20 surrounds the anode and cathode. A casing 22 provides an outer cover for the battery. Optionally, the cathode acts as the casing. Conductor leads 30 and 32 connect the anode and the cathode, respectively with an electrical circuit (not shown) in which the battery is used. While FIGURE 1 shows both the anode 10 and the cathode 12 as comprising a dendritic sponge, it should be appreciated that either the anode or the cathode could be formed without the dendritic sponge.

As long as the foil sheets are reasonably close together, preferably less than a few centimeters apart, the electrolyte will have a low enough resistance that the battery will have an extremely high power density. The equivalent series resistance (ESR) of a battery (R) is obtained by the formula:

$$R = R_{AE} + R_{CE} + R_E + R_A + R_C,$$

where: R_{AE} is the ESR of the chemical reaction between the anode and the electrolyte,

5 R_{CE} is the ESR of the chemical reaction between the cathode and the electrolyte.

R_F is the resistance of the electrolyte,

R_A is the resistance of the anode, and

R_c is the resistance of the cathode,

10 R_{AF} , R_{CE} , and R_E are all dependent on surface area. R_{AE} is inversely proportional to the surface area of the anode/electrolyte interface, or the surface area of the anode. R_{CE} is inversely proportional to the cathode surface area.

$$15 \quad R_E = \rho \frac{A_p}{l}$$

where: ρ is the resistivity of the electrolyte;

20 A_p is the projected surface area of the substrate; and,

t is the width of the electrolyte layer, i.e., the spacing between the anode and the cathode.

The resistances of the anode and cathode are typically small and thus
25 negligible when compared with the other resistances.

FIGURES 2, 3, and 4 show various structures of the dendrites **18**. In a preferred reaction surface **36**, the dendrites are preferably perpendicular or near perpendicular to the substrate **14** to minimize electrical resistance. Between the dendrites are open pores **37**, which provide access to reactants, such as electrically charged species, in the case of a battery, or reactants which are to undergo a catalyzed reaction on the surface, in the case of catalytic surfaces. The dendrites may in turn have smaller, or secondary dendrites **38** growing from the surfaces to increase further the surface area per unit substrate area, as shown in FIGURE 3. The directionally grown dendrites have a high length to width

ratio and are closely and relatively evenly spaced for maximizing the surface area. As shown in FIGURE 2, the dendrites may be coated with a thin layer of a surface material 39, which provides improved electrical conductivity. Or the surface material may provide a reaction surface 36 which acts as a catalyst in applications where the reaction surface catalyzes a reaction.

The directionally-grown dendrites provide a high surface to volume ratio and good surface accessibility. The accessibility is important for electrical properties and for migration of reactants and reaction products in that the conduction paths created are relatively short and tend to be in parallel. The accessibility also improves purification of the sponge, in that unwanted materials are readily removed from the interdendritic spaces. For electrical devices, the accessibility allows an electrolyte to infiltrate the sponge for complete filling of the sponge.

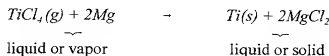
The reaction surface (36) is well suited to use in catalyzed reactions. Catalysts are substances which increase the speed of chemical reactions. The reactants are usually in the form of gas or vapor or liquid. The present application pertains to such reactions in the presence of solid catalyst. It is beneficial for the acceleration of the chemical reaction that the catalyst has a high surface area and that this surface area is readily accessible to the reactants. These desired conditions are best met with a directional dendritic sponge, as shown in FIGURES 2-4, although non-directional sponges may also be used. The sponge is either the catalyst itself or it is the carrier of a catalyst substance that is attached to the sponge surface. The desired conditions for acceleration of reactions are also met with a sponge that has readily accessible pores and especially with a thin layer of sponge that allows the reactants to flow through open ended pores with little resistance. The pores of directional or non-directional sponge layers preferably have relatively direct and open passageways. The sponge layer may be on a substrate, such as wire, foil, ribbon or other provided shape, or it may be free-standing. Its pores are open-ended towards at least one side of the layer, or the pores are open ended through the thickness of the layer. Sponges made by the methods described herein generally have these desired properties. They are, therefore, especially well suited to serve as a catalyst or to serve as a carrier for a catalyst. Suitable metals for catalyst sponge materials or surface catalyst layer 39 include: Li, Be, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Sr, Y, Zr, Nb, Mo, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Rh, Os,

Ir, Pt, Au, Tl, Pb, Bi, Po, and combinations thereof.

Dendritic Sponge Formation

To form the directional sponge, the dendrites are directionally-grown on the substrate material. Several methods are available for forming the dendritic sponge. Three processes have been found to produce particularly uniform dendrites of large surface area. In the first process, a chemical method, a metal halide in vapor form is reduced by a reducing agent, preferably an alkali or earth alkali metal, such that the dendrites of the reduced metal are deposited onto a substrate material.

The metal halide is one which is gaseous at the reaction temperature. Several metal halides have been found to be suitable. These include chlorides, fluorides, and iodides of titanium, aluminum, tantalum, niobium, zirconium, vanadium, chromium, silicon, germanium, and mixtures of these. For example, in the case of a titanium sponge formed by the reduction of titanium chloride with magnesium, the deposition process can be described by the following equation:



The reaction products are solid titanium and magnesium chloride, which may be liquid or solid, depending on the temperature used.

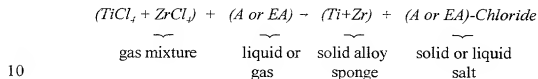
Because of the coexistence of the two reaction products, in this case titanium metal and magnesium chloride, the sponge morphology that develops consists of titanium dendrites with magnesium chloride residing in the inter-dendritic spaces. The magnesium chloride, or other alkali metal halide, is removed by draining and vacuum distillation, or by leaching. Vacuum distillation ensures that residual traces of magnesium chloride are removed so that they do not contaminate the sponge. Preferably, the distillation is carried out at between 800 and 1200°C at a high vacuum to ensure complete removal of the alkali metal halide.

Magnesium and sodium are particularly preferred reducing agents, with sodium being the most preferred because of the easier removal of sodium chloride. Additionally, using sodium as the reducing agent allows selection of the level of coarseness

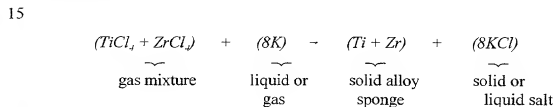
-10-

or fineness of the sponge. Very fine sponge can be made at a relatively low temperature (600-700°C).

Mixed sponges may also be formed by this process. For example, a Ti-Zr alloy sponge may be formed by the reduction of a mixture of $TiCl_4$ and $ZrCl_4$ with an alkali (A) or earth alkali (EA) element. The sponge synthesis process proceeds by the reaction:



A specific example for forming a sponge of 50 atom % Ti and 50 atom % Zr alloy using potassium as the reducing element is:



FIGURES 5 and 6 illustrate the process of depositing the dendrites 18 onto the substrate 14. The process is described with particular reference to the formation of a titanium sponge by reduction of titanium chloride with sodium. It should be appreciated, however, that the process is also suited to the formation of other metal sponges with different reducing agents. The process conditions will vary, depending on the vapor pressure of the reducing metal, and other reaction variables.

A reaction vessel 40 for carrying out the sponge formation process defines a chamber 42. The substrate 14 is supported within the chamber 40 by electrically conducting connectors 44 and 46. A power supply 50 is connected across the connectors for heating the substrate to a suitable reaction temperature.

A reservoir 52 within the chamber contains sodium, or other reducing metal, to provide a vapor pressure of the reducing agent within the chamber. The vapor pressure generated is dependent on the temperature of the chamber. For example, at 520°C, the vapor pressure of sodium is 10^{-2} atmospheres. A heating source 54 surrounds the chamber for heating the chamber to a suitable temperature for providing the vapor.

The heating source 54 is first energized and the chamber brought to the desired temperature for vaporizing the reducing agent. For a sodium reducing agent, a suitable chamber temperature is 705°C, although other temperatures can also be used. The power supply 50 is then energized to resistance heat the substrate 14 to a selected deposition temperature. Typically, the deposition temperature is higher than the temperature of the chamber, such that the deposition of titanium takes place primarily on the substrate. The heated substrate provides a limited number of nucleation sites for growth of dendrites.

Once the desired chamber and substrate temperatures have been achieved, a source of a halide of the sponge material 60, such as a source of titanium chloride, supplies titanium chloride to the chamber 42 through an inlet 62. An inlet valve 64 between the source 60 and the inlet 62 allows the rate of introduction of titanium chloride to be regulated. At the temperature and pressure of the chamber, the titanium chloride is in the form of a vapor which is reduced by the sodium at the surface of the heated substrate. A directionally outward-growing dendritic sponge of titanium dendrites with sodium chloride in the interdendritic spaces is formed. The exact microstructure of the sponge will depend on the number of the nucleation sites on the substrate and on the processing parameters, namely the vapor pressure of sodium, P_{Na} , the vapor pressure of titanium chloride, P_{TiCl_4} , and the reaction temperature.

Chamber temperatures of 100 - 1,000°C are suitable for the formation of a titanium sponge in this manner. A particularly preferred temperature is below 800°C. The rate of growth and shape of the dendrites is dependent on the temperature. At lower temperatures, the dendrites are fine with large surface areas. However, the growth rate is relatively slow. At higher temperatures, the growth is much faster, but the dendrites are wider and thus have a smaller surface area to volume ratio. Thus the surface area of the sponge can be selected for the desired properties of reaction surface.

Once a suitable growth of sponge has been achieved, the unwanted reaction product, sodium chloride in this case, is removed by vacuum distillation, as shown in FIGURE 6. A vacuum pump valve or outlet valve 66 connects an outlet of the reaction vessel to a source of vacuum (not shown), such as a pump. The inlet valve 64 is closed to stop the supply of titanium chloride into the chamber 42 and the source of sodium 52 is preferably sealed or removed from the chamber to prevent unnecessary wastage of sodium. The vacuum pump valve 66 is opened and the temperature of the chamber adjusted to a

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suitable distillation temperature. The vacuum pump draws the sodium chloride from the interstices in the sponge and out of the chamber. Because of the regular orientation of the dendrites, removal of the sodium chloride is readily achieved from essentially all the surfaces of the sponge. No enclosed pores are created which would trap the sodium chloride.

The time needed for distillation depends on temperature and on the length and width of the gas diffusion paths from the interdendritic regions. The vapor pressure of sodium chloride in atmospheres is given by the following equation:

$$\log(P_{\text{NaCl}}) = -12,440 T^{-1} - 0.90 \log T - 0.46 \times 10^{-3} T + 11.43$$

where T is the temperature in degrees Kelvin. The vapor pressure of sodium chloride ranges from 4×10^{-5} to 1.9×10^{-2} atmospheres in the 800 to 1,000 degree temperature range. Complete removal of the sodium chloride by vacuum distillation is thus readily achieved.

A second process for forming the dendritic sponge is a solidification method. In this method, the sponge is deposited from a mixed liquid formed by heating the material for the sponge with an insoluble substance to a temperature at which both the sponge material and the insoluble substance are liquid. Upon solidification, a heterogeneous solid is obtained. The method is particularly suited to the formation of aluminum sponges. Table 1 lists combinations of materials for forming the sponge. The insoluble substance is one which is insoluble in the sponge material selected. It may be an element, or a salt.

Table 1

Materials from which Fine Solidification Structures may be made for Reaction Surfaces

5	Sponge Material	Insoluble Substance Removed From Solidified Structure
	Al, Be, Cd, Zn, Mg, Sn, Pb, Zn, Cu, Ag, Si, Ge, Sb, Tl, Bi, and rare earth elements with melting points below about 1200°C	Li, Na, K, Rb, or Cs
10	Alloys of Mg, Al, Si, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Tl, Pb, Bi	Li, Na, K, Rb, Cs
	Ti, Ti-Be alloy	Ca, Sr, Ba, Li
	Zr, Hf, V, Nb, Ta, Cr, Mn, Fe, Co, Ni, Au, Pt	Ca, Sr, Ba, Li
	Ti, Zr, Hf, V, Nb, Ta, Cr, Mn, Fe, Co, Ni, Be, Au, Pt	alkali or earth alkali halides
15	Pb, Li, Sn, Cd, Ga, In, and alloys thereof	oil

The heated mixture of mutually insoluble materials is allowed to cool. It may be subjected to freezing temperatures to speed solidification. The mixture solidifies with a dendritic structure such that part of the solid consists of the sponge material and the interdendritic spaces consist of the insoluble material. The higher the cooling rate the finer will be the dendrite structure and the greater will be the sponge's surface area per unit substrate area. For example, a mixture of aluminum and potassium solidifies as an aluminum dendrite structure with the interdendritic spaces consisting of potassium. The potassium can be removed, for example, by vacuum distillation leaving an aluminum dendritic skeleton.

The sponge grown by the solidification process may be grown as directionally solidified dendrites on a provided substrate **82** as shown in FIGURES 7A, 7B, and 7C, or extruded as ribbon, as shown in FIGURES 8 and 9. The directionality of the solidification can be further enhanced by providing a temperature gradient, one in which the substrate is cooler than the growing dendrite.

In the embodiment of FIGURE 7, a cold metal substrate **82** is dipped into well-mixed molten mixture **84** of a liquid sponge material **86** and a liquid insoluble material **88**. As seen in FIGURES 7B and C, dendrites of the sponge material **86** grow on the

substrate in a directional manner generally perpendicular to the substrate surface. The insoluble material **88** is rejected into the interdendritic space.

In the embodiments of FIGURES 8, 9, and 10, the molten mixture of sponge material and insoluble material is brought into contact with a rotating heat sink. As shown in FIGURE 8, the mixture **90**, heated by a heating coil **92**, is allowed to flow through a narrow aperture **94** onto a rotating cylindrical heat sink **96**, such as a chilled roller, positioned below the mixture. As the heat sink rotates, a ribbon **98** of solidified sponge material forms. As shown in the enlarged section of FIGURE 9, the dendrites **100** in the ribbon grow away from the side closest to the heat sink, with a continuous layer **102** of the sponge material closest to the heat sink. The layer **102** acts as the substrate for supporting the dendrites. As before, the insoluble material **104** is removed from the interdendritic spaces by vacuum distillation.

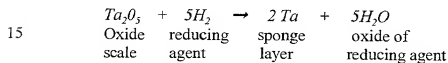
In the embodiment of FIGURE 10, a rotating cylindrical heat sink **108** contacts a bath **110** of the mixture **112** of sponge material **114** and insoluble material **116**. Optionally, a stirrer **118** in the bath keeps the sponge material and insoluble material well mixed. As the heat sink rotates, a layer of the mixture adjacent the sink cools and a ribbon **120** forms. As with the embodiment of FIGURES 8 and 9, the dendrites of the sponge material **114** grow away from the surface of the heat sink and the insoluble material concentrates in the interdendritic spaces.

For the solidification process, the material for the sponge preferably has a melting point which is below about 1,700°C, and more preferably below 1200°C, for ease of processing. Optionally, the sponge material may be an alloy of one or more of the following elements: Mg, Al, Si, Zn, Ga, Ge, Be, Li, Ni, Au, Pt, Cu, Ag, As, Se, Cd, In, Sn, Sb, Ti, Pb, Bi, and rare earth elements.

A third process for forming the dendritic sponge is an oxidation/reduction method. In a first step, an oxide scale is grown on a suitable substrate. With reference to FIGURES 11A, 11B, 11C, and 11D, the substrate **120** may be in the form of a sheet, strip, wire, mesh, or fabricated skeleton of a metal, such as Ti, Ta, or alloys of Ti-Ta, Ti-Zr, or Ti-Be. The thickness of the scale **122** is preferably between 0.5 micrometers and 10 millimeters. The metal is one which has an oxide with a Pilling-Bedworth ratio of greater than 1. When this is the case, the molecular volume of oxide scale **122** produced is greater

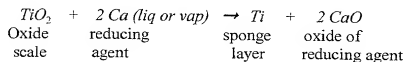
than the volume of the metal **124** consumed (compare FIGURES 11B and 11A). For tantalum, for example, which has a Pilling-Bedworth ratio of 2.5, the oxide layer is at least 2.5 times the thickness of the metal consumed. The scale may be grown to an extent at which either all or just a portion of the substrate is converted into oxide scale. The thickness of the scale is preferably 1 to 10^4 times the desired pore size of the metal sponge to be formed.

In a second step, shown in FIGURES 11C and 11D, the oxide scale is reduced at high temperature to the metal **126** with a suitable reducing agent **128**. For oxides of the metals Ti, Ta, Zr, Be, or their alloys, reducing agents, such as Li, Mg, Ca, Ba, Sr, and hydrogen are effective. The reducing agent **128** is preferably in the form of a gas or liquid. For example, tantalum oxide scale may be reduced to tantalum sponge in the presence of hydrogen as follows:



Similarly, a titanium oxide scale may be reduced to a titanium sponge with calcium as follows:

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Since the reduced metal has a smaller volume than that of the oxide scale, the reduced metal is porous. Accordingly, during the reduction reaction, the oxide layer is transformed into a metal sponge with generally directional pores **130**, shown in FIGURES 11C and 11D, extending from the outside of the reduced metal towards the substrate/reduced metal interface. The pores contain the oxide of the reducing agent, for example, water vapor in the case of hydrogen and calcium oxide in the case of calcium. The oxide may be leached out, for example, with water or an acid, such as acetic acid. In the case of water as the oxide, the water is preferably carried off as vapor. The remaining metal sponge has many of the properties of the outwardly grown sponges prepared by the first and second methods. The sponge has a high surface area with an easily accessible open porosity.

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Where only part of the substrate is turned into the oxide scale and then into a metal sponge, the remaining substrate provides a path of high electrical conductivity. The substrate thus feeds or receives electrical current to or from the dendrites. A path of high electrical conductivity is important for batteries, and other electrical applications.

5

Reaction Surfaces Employing Non-Directionally-Grown Sponges

Non-directionally grown sponges are sponges in which the pores are oriented in random directions or may have directional character within a given grain. As with the directional sponges, the pore widths are chosen depending on the application, for example, 10 the power density desired or the reaction products formed. Preferably, the pores consist of interconnected channels having a width of from about 10 nm to 100 μm , or more.

Several methods exist for forming the reaction surface. In a first method, a thin layer of particles of the sponge is bonded to a substrate, such as a metal strip. The layer of sponge particles is preferably less than 2 cm in thickness and may be as thin as 1 μm , or 15 less. In a second method, a non-directional sponge is grown on a substrate.

In one preferred embodiment, the reaction surface is used as a battery electrode. FIGURE 12 shows a battery **138** in which an anode **140** (the reaction surface) comprises a metal strip **142** to which a surface layer of electrically conductive metal sponge particles **144** is attached by sinter-boding, or other suitable method. The battery also includes a cathode 20 **146**, which forms the outer casing of the battery, and an electrolyte **148** which penetrates the pores of the sponge particles to contact the large surface provided by the sponge for electrochemical reactions. A bead **150** of an insulation material separates a terminal **152** for the anode from the adjacent cathode.

Obviously, both the anode and the cathode may be formed from particles of 25 the sponge, or just one of the electrodes. When both are formed from the sponge particles, the sponge particles may be formed from the same material or different materials.

FIGURES 13-14 show different embodiments of a battery, in which the electrodes include interdigitated metal strips. In the embodiment of FIGURE 13, a battery **158** includes an anode **160** having a series of conductive metal strips **162**. Sponge particles 30 **164** are sintered on to upper and lower surfaces of the strips in the form of a thin layer **166** of the particles. A cathode **168** comprises metal strips **170** without sponge particles.

In the embodiment of FIGURE 14, a battery **180** is formed in which both

anode 182 and cathode 184 include metal strips 186, 188 with sintered sponge particles 190,192, respectively. The anode and cathode sponge particles are preferably formed from different materials.

FIGURE 15 shows a battery 200 in which the anode 202 includes a surface layer 204 of non-directional sponge which has been formed on a substrate material 206 by a scale growth and reduction method. The cathode 208 may be similarly formed or comprise metal strips 210, as shown in FIGURE 15.

Other combinations for the anode and cathode are also contemplated. For example, one of the anode and cathode may be formed from a non-directional sponge, while the other is formed from a directional sponge. The electrodes may be formed from sponges having different porosities, or formed from different materials. The sponges may be formed by the same or different processes.

Formation of Non-Directional Sponges

As for directional sponges, a number of methods are available for forming the non-directional sponges. In a first method, chemical vapor deposition is used, as described for the directional sponges, but with some modifications. Specifically, a metal halide, in vapor form, is reduced by a reducing agent, preferably an alkali or earth alkali metal. A sponge of the reduced metal grows non-directionally in the reaction chamber. This is achieved by eliminating the substrate material altogether, or by depositing the sponge onto a substrate material without controlling the direction of growth of dendrites. As with the directionally-grown sponges, the unwanted reaction product, such as sodium chloride, is leached out by vacuum distillation, as shown in FIGURE 6, or by other suitable methods.

In a second method, the sponge is grown by a solidification method, in a manner similar to that described for the directionally-grown sponges. In this case, however, the sponge made by the solidification process is grown as a random sponge where guidance is absent during the solidification process. The two insoluble materials are allowed to cool in the absence of a substrate, so that a non-directional sponge forms with the unwanted reaction product in the pores of the sponge. The unwanted reaction product is then removed as for the directional sponge. The directionally solidified sponge is preferred over the non-directional sponge, however, since the insoluble interdendritic material is readily removed, there are few inaccessible areas, infiltration of the electrolyte or reactants is easier, and the internal resistance is lowered.

In a third method, sponge particles are formed by reduction of particles of an oxide to the sponge material, or by reduction of a layer of oxide grains. This is similar to the scale reduction method shown in FIGURE 15. However, the grains may consist of loosely bonded or sintered oxide particles. For example, a substrate, such as iron, nickel, or tin, is coated with a slurry formed from a binder material and oxide particles, such as iron oxide, nickel oxide, or titanium oxide. The coated substrate is heated to remove the binder material. Then the surface is reduced with a suitable reducing agent, such as H_2 , CO, or Ca. A layer of metal sponge particles (non-directional) is thereby sintered or loosely bonded to the surface.

The non-directional sponge particles are then adhered to a suitable substrate material by sintering, or other suitable adhering technique.

Having thus described the preferred embodiment, the invention is now claimed to be:

1. A battery (1, 138, 158, 180, 200) comprising an anode (10, 140, 160, 182, 202), a cathode (12, 146, 168, 184, 208), and an electrolyte (20, 148) therebetween, the
5 battery characterized by:

at least one of the anode (10, 140, 160, 182, 202) and cathode (12, 184, 208) comprising an electrically conductive sponge material (16, 114, 164, 204).

2. The battery of claim 1, further characterized by:

the at least one of the anode and cathode comprising an electrically conductive substrate (14, 82, 102, 120, 142, 162, 186, 188, 206) which is in electrical contact with the electrically conductive sponge material.

3. The battery of claim 2, further characterized by the substrate being in the form of a foil (14), wire, ribbon (98, 102, 120), cast structure, or sheet (14, 82).

4. The battery of either one of preceding claims 2 and 3, further characterized by the substrate and the electrically conductive sponge being formed from the same material.

5. The battery of either any one of preceding claims 2 -4, further characterized by the substrate including a metal selected from the group consisting of silver, copper, and aluminum.

6. The battery of any one of preceding claims 2-5, further characterized by the sponge material being in the form of particles (144, 164, 190, 192) attached to the substrate.

7. The battery of any one of preceding claims 2-5, further characterized by the sponge material (16, 86, 98, 114, 120) being in the form of a layer (122, 204) of sponge grown on the substrate.

8. The battery of either any one of preceding claims 1-7, further characterized by:

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the at least one of the anode (**10, 160, 182, 202**) and cathode (**12, 168, 184, 208**) comprising a plurality of thin layers (**166**) of the electrically conductive sponge material.

9. The battery of any one of preceding claims 1-8, further characterized by:
the electrically conductive sponge material including an element selected from the group consisting of copper, silver, gold, aluminum, and combinations thereof.

10. The battery of any one of preceding claims 1-9, further characterized by the electrically conductive sponge material defining dendrites (**18, 100**).

11. The battery of claim 10, further characterized by the dendrites having a width of from about 200 nanometers to 30 micrometers.

12. The battery of either one of claims 10 and 11, further characterized by the at least one of the anode and cathode including at least one substrate layer (**14, 82, 206**) and wherein the dendrites (**18, 100**) extend from the substrate.

13. The battery of claim 12, further characterized by the dendrites (**18**) extending generally perpendicularly from the substrate layer (**14**).

14. The battery of any one of claims 1-13, further characterized by the sponge material being coated with an electrically conductive material (**39**).

15. A method of conducting a reaction on a surface, the method comprising forming the surface (**36**), contacting the surface with a reactant, and allowing the reaction to take place, the method characterized by:

the step of forming the surface including:

5 growing a sponge material (**16, 114, 164, 204**) having a plurality of open pores (**37, 130**) which are accessible to the reactant.

16. The method of claim 15, further characterized by the sponge material including one of the group consisting of Li, Be, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Co.

Ni, Cu, Zn, Ge, Sr, Y, Zr, Nb, Mo, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Rh, Os, Ir, Pt, Au, Tl, Pb, Bi, Po, and

5 combinations thereof.

17. The method of either one of claims 15 and 16, further characterized by:
the step of growing the sponge including:

reducing a compound (122) to its elemental form (126), the elemental
form occupying a smaller volume than the compound such that an open
5 porous structure is formed.

18. The method of claim 17, further characterized by the step of growing the
sponge including:

heating a substrate (14) to a deposition temperature;

contacting the substrate with a vapor which includes a halide of the sponge material
5 in the presence of an alkali or earth alkali metal vapor, the sponge halide vapor reacting with
the alkali or earth alkali metal vapor to form the sponge material and an alkali or earth alkali
metal halide, the sponge material being deposited on the substrate in the form of dendrites
(18).

19. The method of claim 18, further characterized by:

removing the alkali or earth alkali metal halide from the sponge material by vacuum
distillation.

20. The method of claim 15, further characterized by the step of growing the
sponge including:

heating the sponge material (86, 114) with an insoluble material (88, 116) to a
temperature at which the sponge material and the insoluble material are both liquids, the
5 sponge material and the insoluble material being mutually insoluble at a temperature at
which the sponge material freezes;

mixing the two liquids;

cooling the sponge material and the insoluble material to form the sponge; and
removing the insoluble material from the sponge.

21. The method of claim 20, further characterized by the step of cooling including:

cooling the sponge material (86) and the insoluble material (88) adjacent a substrate (82) to form a directionally grown sponge of the sponge material on the substrate.

22. The method of either one of claims 20 and 21, further characterized by the sponge material comprising an element selected from the group consisting of Mg, Al, Si, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Cv, Ag, Ti, Te, Tl, Pb, Bi, and alloys thereof.

22. The method of claim 21, further characterized by the insoluble substance being selected from the group consisting of Na, K, Rb, Cs, Ca, Sr, Ba, and salts thereof.

23. The method of claim 17, further characterized by the step of growing the sponge material including:

forming an oxide scale (122) on a substrate (120), the substrate including a metal which is oxidizable to an oxide having a lower density than the substrate, by oxidizing at
5 least an outer portion (124) of the substrate to form the oxide scale; and
reducing the oxide scale to the metal, the metal having an open porous structure.

24. The method of claim 23, further characterized by the step of reducing including:

reducing the oxide with a reducing agent (128); and
the method further including after the step of reducing:
5 removing an oxide of the reducing agent from the porous metal.

25. The method of claim 24, wherein the oxide of the reducing agent is a fluid.

26. A metal sponge with high specific surface area that is accessible to reactants with reaction paths that are no larger than two times the sponge thickness.

27. A metal sponge with a geometry of open porosity between dendrites that enables through-flow of gas or liquid with an electrical resistance that is at least two times less than that of an ordinary sintered powder sponge.

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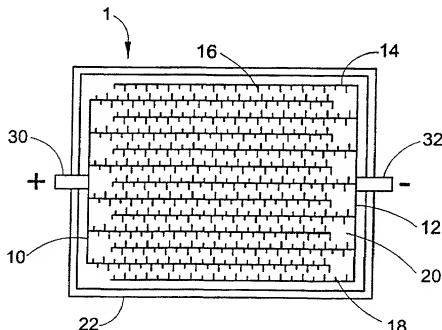
Published

With international search report.

(54) Title: METAL SPONGES FOR RAPID SURFACE-CHEMICAL REACTIONS

(57) Abstract

Surfaces suited to performing chemical reactions thereon are provided by a sponge material (16) having fine dendrites (18). The sponge material may be formed by growing the dendrites on a substrate (14) or particles of the sponge material may be sintered onto a substrate. The sponge material is suitable for use as an anode (10) or a cathode (12) in a battery (1). The sponge material may be coated with another material, which acts as a catalyst, or which improves the electrical conductivity of the sponge.



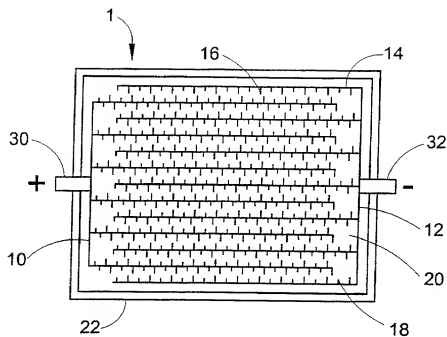


FIG. 1

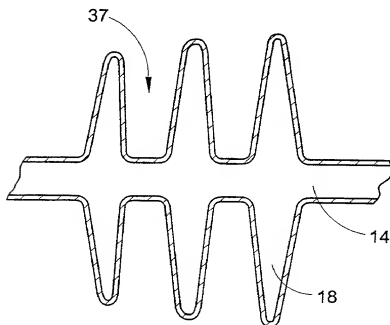


FIG. 2

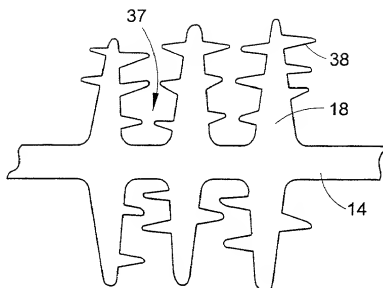


FIG. 3

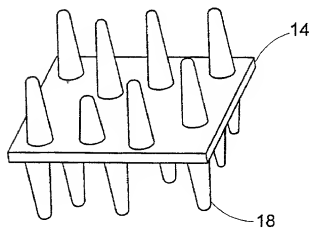


FIG. 4

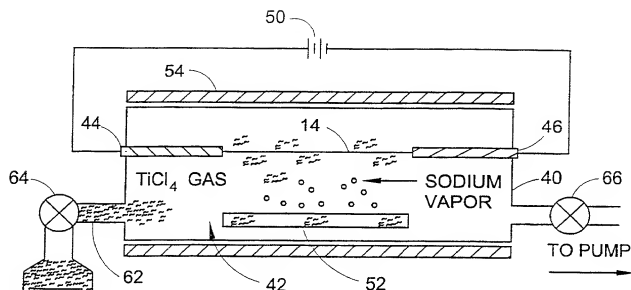


FIG. 5

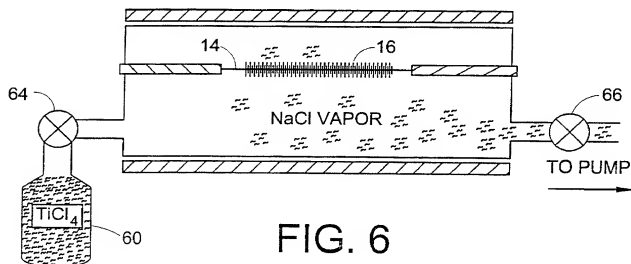


FIG. 6

FIG. 7A

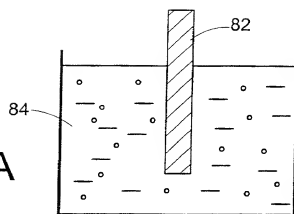


FIG. 7B

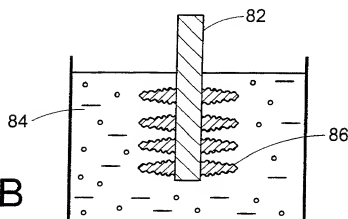
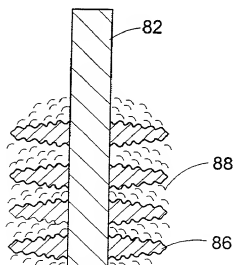
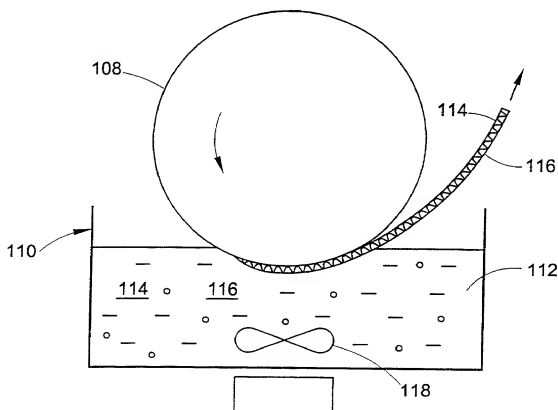
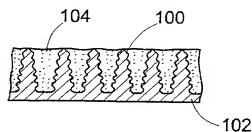
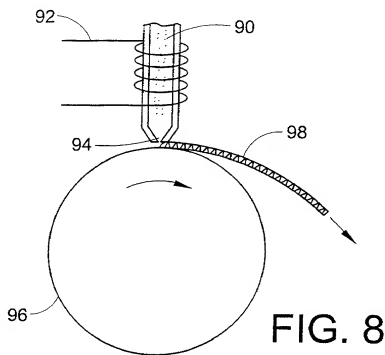


FIG. 7C





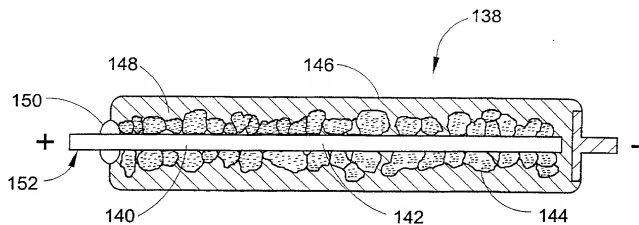


FIG. 12

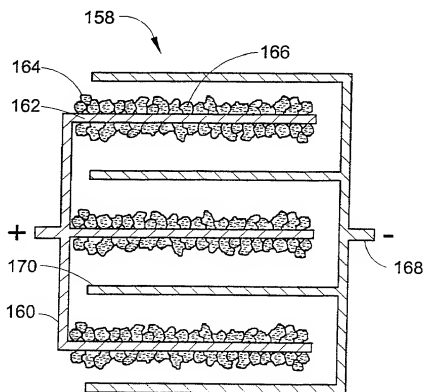


FIG. 13

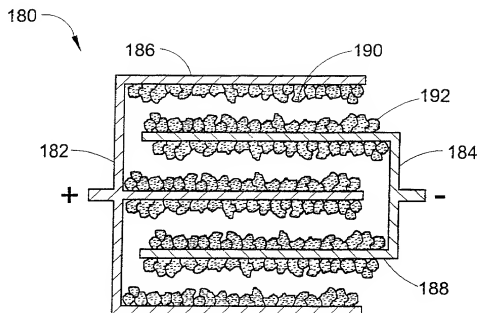


FIG. 14

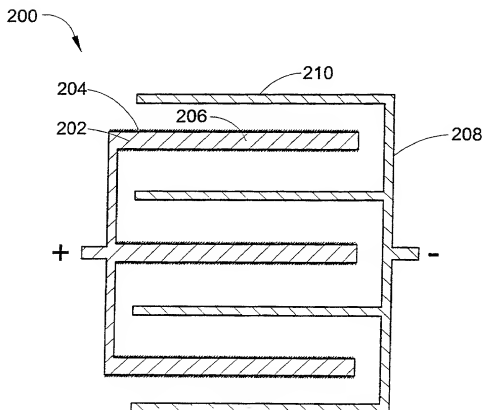


FIG. 15

DECLARATION AND POWER OF ATTORNEY
FOR UTILITY PATENT APPLICATION
 (37 CFR 1.63)

As a below inventor, I hereby declare that:

My residence, mailing address and citizenship are as stated below next to my name.

I believe I am the original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METAL SPONGES FOR RAPID SURFACE-CHEMICAL REACTIONS

the specification of which

☐ is attached hereto

or

☒ was filed on September 13, 2001, as United States Application Number 09/914,517.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent or inventor's certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application(s) for patent or inventor's certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application Number(s)	Country	Foreign Filing Date	Priority Not Claimed	Certified Copy Attached? YES NO
PCT/US00/06724	WIPO	March 15, 2000		<input type="checkbox"/> <input type="checkbox"/>

I hereby claim the benefit under 35 U.S.C. 119(e) of an United States provisional application(s) listed below.

Application Number(s)	Day/Month/Year Filed	Additional Provisional Application Numbers Listed on Supplemental Priority Data Sheet Attached
60/124,443	March 15, 1999	N/A

I hereby claim the benefit under Title 35, United States, § 120 of any United States application(s) or any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International

09/14/517, 09/29/02
20020929

application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information which is material to patentability as defined in Title 37, of Federal Regulations Code, § 1.56(a) which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Parent Application or PCT Parent Number	Parent Filing Date Day/Month/Year Filed	Parent Patent Number (if applicable)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorneys to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the APPLICATION or any patent issued thereon.

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